



***THE IMPACT OF ENERGY
AND ENVIRONMENT
ON THE SCIENCE AND
TECHNOLOGY OF GLASS***

ABSTRACTS

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** Istituto di Fisica dell'Università, Unità GNSM-CNR, Padova, Italy	
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** National Research Council Canada, Montréal, Québec, Canada

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* Glass Containers Corporation, Knox, Pennsylvania, U.S.A.

** University of Colorado, Colorado Springs, Colorado, U.S.A.

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² Department of Chemistry, Washington & Lee University, Lexington, Virginia, U.S.A.	
³ Department of Geology, Washington & Lee University, Lexington, Virginia, U.S.A.	
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1. Ontario Research Foundation, Mississauga, Ontario, Canada.	
2. Defense Research Establishment Pacific, Victoria, British Columbia, Canada	

SESSION I

RECENT DEVELOPMENTS IN GLASS SCIENCE
AND TECHNOLOGY

THE ELECTRONIC CONDUCTION OF $\text{ZnO-TeO}_2\text{-V}_2\text{O}_5$, $\text{BaO-TeO}_2\text{-V}_2\text{O}_5$ AND $\text{P}_2\text{O}_5\text{-TeO}_2\text{-V}_2\text{O}_5$ GLASSES

Yoshida, T., Hirashima, H., Ito, A., Mori, A., and Yokota, H.

Keio University, Yokohama, Japan

To elucidate the electronic conduction of the glasses containing V_2O_5 and TeO_2 the glasses of the system $\text{ZnO-TeO}_2\text{-V}_2\text{O}_5$ have been studied and compared with the system $\text{BaO-TeO}_2\text{-V}_2\text{O}_5$ and $\text{P}_2\text{O}_5\text{-TeO}_2\text{-V}_2\text{O}_5$.

The conductivity depended mainly on the amount of V_2O_5 . The increase of conductivity was nearly proportional to the decrease of the activation energy for conduction with the inclination of $1/kT$. Therefore, the conduction was considered to proceed by the small polaron hopping between $\text{V}^{4+}\text{-O-V}^{5+}$ pairs as proposed by N. F. Mott.

In the glasses $x\text{ZnO} \cdot (0.5-x)\text{TeO}_2 \cdot 0.5\text{V}_2\text{O}_5$ the logarithms of conductivity decreased from -2.79 to -4.90 and the activation energy increased from 0.33 to 0.43 eV as x increased from 0.1 to 0.5 (150°C). The mean distance between vanadium ion pairs, $a_{\text{V-V}}$, calculated from the observed density and thermal expansion coefficient, changed a little by this substitution and decreased from 4.17 to 4.07 Å. When TeO_2 was substituted by V_2O_5 in the $x\text{V}_2\text{O}_5 \cdot (0.8-x)\text{TeO}_2 \cdot 0.2\text{ZnO}$ glasses, the logarithms of conductivity increased from -5.23 to -3.69 and the activation energy decreased from 0.41 to 0.37 eV which corresponded to a decrease of $a_{\text{V-V}}$ from 4.53 to 3.94 Å.

The conductivity of the glasses with the same amount of V_2O_5 was maximum in the system $\text{V}_2\text{O}_5\text{-TeO}_2$. The substitution of P_2O_5 , ZnO and BaO for TeO_2 decreased the conductivity. The degree of the decrease increased in the order of P_2O_5 , ZnO and BaO . However, $a_{\text{V-V}}$ changed a little by these substitutions. The maximum change was about 0.2 Å in the $\text{P}_2\text{O}_5\text{-TeO}_2\text{-V}_2\text{O}_5$ system. Therefore the variation of the conductivity and the activation

energy could not be elucidated by the change of a_{V-V} proposed by H.F. Mott. Other factors such as the change of the polarisability were considered to be effective. The polarisability should be maximum in TeO_2 and should decrease in the order of P_2O_5 , ZnO and BaO . The activation energy depends mainly on the polarisability in these glasses.

INVESTIGATIONS OF ANTIREFLECTIVE LAYERS OBTAINED BY ION IMPLANTATION ON FLAT GLASS

Geotti-Bianchini, F.^(*), Lo Russo, S.^(**), Mazzoldi, P.^(**),
Nicoletti, F.^(*), and Polato, P.^(*).

(*) Staz. Sperim. del Vetro, Murano (Venice), Italy

(**) Istituto di Fisica dell'Università, Unità GNSM-CNR,
Padova, Italy

A significant improvement in the overall efficiency of solar energy converters is achieved by minimizing the solar transmittance losses of glass coverplates. The results of optical, chemical and microscopical investigations are reported with reference to antireflective layers obtained by Ar^+ ion implantation on a soda-lime flat glass. The antireflective effect is due to the appearance of an interferential layer with a perturbed refractive index as compared to bulk glass and can be enhanced by choosing a suitable range of energies and implanted doses. At a constant current density of 2 microamperes/sq. cm., the implantation energies and doses were varied between 40-100 keV and 10^{15} to 10^{17} Ar^+ ions/sq.cm., respectively. The transmittance and specular reflectance curves obtained in the solar spectral range are presented and the energetic transmittance and reflectance are compared to those of the unimplanted sample.

Thickness and refractive index of the perturbed layers were investigated as a function of doses and energy. The sodium depth profile was measured by using the $\text{Na-23} (\text{P}, \alpha) \text{Ne-20}$ nuclear reaction. It shows the presence of a sodium depleted layer, whose thickness has been compared with the optical results.

If energies are increased above 50 keV, the implanted surface swells and damage appears. A sharp step between the implanted and unimplanted surface was observed. Its height was measured with an interferometric microscope and correlated with the thickness of the perturbed layer. The morphology of the surface damage (craters, blisters) was examined and the average dimensions of the holes were evaluated by

scanning electron microcopy. The samples with implantation energies higher than 50 keV show a coloured appearance, due to the combined effect of scattering and interference. In this case, the antireflective effect is superseded by transmission losses due to light scattering. The diffused reflectance and transmittance curves have been correlated with optical and electron micrographs of the perturbed surface.

GLASS-TO-METAL SEALS: RECENT DEVELOPMENTS

Eagan, R.J. and Wilder, J.A.

Sandia National Laboratories,
Albuquerque, New Mexico, U.S.A.

We have extended the use of glasses in hermetic seals by developing glasses and glass-ceramics based on phosphorous pentoxide which seal to high thermal expansion alloys; e.g. aluminum, copper and 300 series steels. Desirable properties include high coefficients of thermal expansion, ($> 180 \times 10^{-7} \text{ }^{\circ}\text{C}^{-1}$), low sealing temperatures ($< 340^{\circ}\text{C}$) and low helium permeability. Depending upon the glass composition, the corrosion resistance of these glasses to water attack varies from extremely hygroscopic to equal to that of currently used commercial silicate sealing glasses when tested by immersing in deionized water at 22°C . We have decreased that rate further by adding nitrogen to the glass by using aluminum nitride as a starting material. These glasses are only 60% the strength of silicate glasses and are somewhat more susceptible to thermal shock. Nevertheless, seals made with these glasses have survived severe thermal cycling, e.g. boiling water to liquid nitrogen. We are evaluating phosphate glasses and glass-ceramics for use in vacuum tubes and electrical connectors.

Lithium ambient temperature cells are desirable power sources because they have a high energy storage density. However, their lifetime has been limited by corrosive attack of the glass insulator used to isolate a refractory metal anode pin from the cathode case. We studied that corrosion process, developed a model to explain it, (the underpotential deposition of lithium) and developed a corrosion resistant glass for the seal. The silicate glass consists of 45 wt% SiO_2 , 8% B_2O_3 , 20% Al_2O_3 and 27% $\text{CaO} + \text{MgO} + \text{SrO} + \text{La}_2\text{O}_3$. It has a thermal expansion coefficient of $55 \times 10^{-7} \text{ }^{\circ}\text{C}^{-1}$ and softening temperatures of 700°C , i.e. it can be sealed in conventional sealing furnaces. The corrosion resistance to Li (e.g. as found in lithium/ SO_2 cells) arises from the relatively large concentration of oxides which will not react with lithium metal. After a 5 month

accelerated test, the electrical resistance of a seal containing this glass is 10^{10} times that of a seal made with a conventional sealing glass.

†This work performed at Sandia National Laboratories, supported by the U.S. Department of Energy under contract DE-AC04-76DP00789.

*A U.S. DOE facility

EFFECTS OF ADMIXTURES ON SINTERING OF HIGH SILICA COLLOIDAL GELS

Rabinovich, E.M., MacChesney, J.B. and Johnson, D.W. Jr.

Bell Laboratories, Murray Hill, New Jersey, U.S.A.

A new method of preparation of silica glass by sintering of colloidal gels has been developed. The process steps include a treatment of amorphous colloidal silica (fumed silica or silica prepared by water hydrolysis of SiCl_4), mixing with water, casting in a mold, gelling, drying and sintering to a transparent (1450°C) or opaque (1250°C) glass. This glass has properties quite identical to those of commercial fused silica (1).

The process of doping of silica glass prepared from this gel is different from the conditions involved in the gel route based on hydrolysis and polymerization of alkoxides. In the latter case the glassy network comprising dopants or modifiers is formed chemically near room temperature. In the case of colloidal silica gels, other oxides may be easily introduced in water-soluble form. The mutual solution and network formation take place only at sintering temperatures, however most of the dopants promote crystallization of amorphous silica. This consideration limits the doping of such silica glass by materials which are amorphous or liquid at the sintering temperature. Suitable dopant materials are exemplified by B_2O_3 , P_2O_5 and GeO_2 .

Boron oxide was introduced as a water solution of H_3BO_3 by one of two ways: a) this solution was used instead of pure water to form colloidal silica gel; b) the dried porous silica structure was impregnated by the solution and then dried again. Due to the limited solubility of H_3BO_3 in water ($6.35\text{g}/100\text{ cm}^3$ at 30°C), more concentrated hot solutions were used for doping levels in the range 4-10% B_2O_3 . Introduction of B_2O_3 sharply reduces the tendency toward crystallization of glass in the course of sintering and facilitates sintering by lowering viscosity. High-silica

glasses in the range of 0 to 8 wt. % B_2O_3 were prepared and studied. The linear coefficient of thermal expansion of pure silica glass is equal to that of commercial fused silica and increases to $12 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$ by introduction of up to 8 wt. % B_2O_3 .

Similarly, phosphorous oxide was introduced by a solution of H_3PO_4 . However both H_3BO_3 and H_3PO_4 tend to migrate through capillaries during drying leading to a non-uniform distribution of B_2O_3 and P_2O_5 in glass. Dopants are concentrated at the surfaces when the water evaporates. A partial solution to this problem consists of cooling and even freezing the cast specimens after gelling, to precipitate the dopants and prevent migration during drying.

Germanium oxide was introduced as a suspension of GeO_2 formed by hydrolysis of $GeCl_4$. Binary GeO_2 - SiO_2 glasses were usually "hazy" but the quality of glasses could be improved by additions of B_2O_3 .

Alkali admixtures led to crystallization of glass in the course of sintering. A similar result was obtained with V_2O_5 , Al_2O_3 and TiO_2 .

The described results show that high-silica glasses containing B_2O_3 , P_2O_5 and GeO_2 can be prepared by sintering at relatively low temperatures.

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VITREOUS COMPOSITIONS BASED ON AMORPHOUS SILICA
IN RICE HUSK ASH

Kumar, S., Agrawal, B.M.

Central Glass and Ceramic Research Laboratory,
Calcutta, India

Ash produced from a particular source of rice husk contained 95.24% SiO_2 essentially in amorphous form, the other constituents being Al_2O_3 - 1.63, Fe_2O_3 - 0.56, CaO - 0.72, MgO - 0.31, K_2O - 1.17, Na_2O - 0.24 and P_2O_5 - 0.04%. The method of production of white ash was standardized and the product was characterised with respect to micro-structure, surface area and chemical reactivity.

Vitrification of rice husk bearing compositions with 5-10% B_2O_3 and 0-10% TiO_2 was studied at temperatures ranging from 1000 to 1400°C. The studies indicated that amorphous silica in ash readily reacts with boric oxide to produce vitreous materials at relatively low temperatures.

Vitreous mass produced from selected compositions was ground and specimens prepared by compaction of the powdered material were sintered in the above temperature range. Sintering kinetics and development of microstructure were studied. The chemical stability and the thermal, mechanical and electrical properties of the sintered specimens were determined. Results were discussed in relation to composition and micro-structure. It has been shown that the agro-waste can be utilised to produce vitreous materials possessing low thermal expansion, adequate mechanical strength and favourable electrical properties.

SESSION II

GLASS: THE NEW FRONTIERS

NON-CRYSTALLINE SOLIDS: THEIR PREPARATION AND STRUCTURE

Roy, R.

The Pennsylvania State University,
Pennsylvania, U.S.A.

The noncrystalline solid state is characterized by two parameters: an a-periodic structure which does not give Bragg diffraction of X-rays, electrons or neutrons, and an excess G which renders it always metastable with respect to some stable crystalline state.

Noncrystalline solids (NCS) can be made by introducing/leaving the excess free energy into each of the three states of matter: solids, liquids and gases. The same composition can exist essentially in an infinite variety of polymorphs grouped into five or six families depending on the origin of the NC-solid, e.g., from liquids by temperature quenching we create glasses, by μ -quenching (= rapid change of chemical potential) we create gels.

The first radical change of the last decade is the enormous expansion of the compositional range of new glasses due to new quenching techniques, of vapor deposited NCS and gels, oxides, metals, semiconductors, etc. This is also compelling evidence that effective quenching rate dominates all variables in controlling NCS-formation. Splat-cooling, sputtering, gel techniques, and laser-flashing have brought us to the place where virtually any solid matter can be obtained in the NCS state. T_x , the crystallization temperature (by very rapid or non-nucleated processes) limits the temperature at which some NCS may be observed. Conversely, the T_x of some materials which cannot be made by conventional techniques is extremely high, making them technologically very interesting. A large number of data on new NCS compositions will be provided.

A second little remarked property of NCS--in sharp contrast to a crystalline phase--will be described. The ability to modify the phase structurally or compositionally after solidification. NCS solids under pressures from a few kb to 500 kb can be quenched with a higher metastable equilibrium density; NCS solids can be "stuffed" with up to 10-15 mol % of fixed gases (H, CO₂, Ar); NCS solids can be annealed (even isoplethally) to give regions of differing structure.

A third frontier in glass science is the abandoning of the random network model as the structure of glass and derivatively of other NCS. It is meaningless to presume to describe the structure of the NCS state of a particular composition (for example, "Amorphous Germanium"), as though it were unique. There exists in principle an infinite number of NCS structures for each composition. A series of metastable equilibrium states depending on the p,t (probably) exist. The use of the Zachariasen model, and the concept of a perturbed crystal, as the departure point for all NCS structure has proved disastrous for both glasses and other NCS. Empirical data from NCS--Si, Ge, S, C, H₂O, and a host of oxide glasses will be presented as the basis for the author's non-uniform or supramolecular heterogeneity model (analogous to Moriya and Porai-Koshits). It will also be shown that the thermodynamics of metastable → stable transformation drives the structure towards heterogeneity. Finally, it will be argued that the aperiodicity boundary condition demands that no structure can be based on data not drawn from a set of tools applicable to the 1-5Å, 3-10Å, 10-100Å ranges. The best candidates for such a set of characterization methods will be reviewed.

THE GLASSY STATE - A MODERN THEORETICAL TREATMENT

Phillips, J.C.

Bell Laboratories, Murray Hill, New Jersey, U.S.A.

Many materials form glasses in addition to the common and familiar oxide glasses. Some of these materials are composed of large organic molecules, some are inorganic chalcogenide analogues of the oxide glasses, while some are even metallic. Some people use the word glass to describe any non-crystalline array of objects such as a spin "glass". Others use the phrase to describe non-equilibrium structures obtained by quenching or evaporation onto cold substrates.

Two approaches to this diverse array of phenomena are in general use. The first or statistical approach attempts to provide a conceptual framework for describing all non-equilibrium phenomena which take place on a time scale comparable to or slower than the laboratory time scale. In this universal approach one speaks of a wide spectrum of relaxation times extending from fractions of seconds to years, depending on sample temperature, etc,

While the statistical approach has the advantage of identifying certain kinds of behavior that are common to all slowly equilibrating systems, it has the disadvantage of being incapable of providing specific insights that can identify the origins of non-crystallinity. These insights can be obtained from experiments that study the electronic and atomic or molecular structure of glasses and compare the similarities and differences to the same materials in crystalline form.

The second approach utilizes the results of many microscopic experiments to construct structural models. Whereas modern crystallographic techniques uniquely determine the atomic structures of most crystalline materials, there is no routine method for establishing glass structures. As a result one often sees the structures of insulating or metallic glasses described in terms of "random" networks or "random" packed spheres, respectively. We know, however, that most pure phases readily crystallize and that the glass-forming tendency is quite rare. Thus this

application of the phrase "random" is mistaken, because it provides no mechanism which can distinguish very good glass-formers from normal rapidly crystallizing materials.

Many recent experiments have provided specific information on the molecular structures of network glasses, both oxide and chalcogenide. Most noteworthy are electron microscope, Raman scattering and nuclear quadrupole resonance measured by Mössbauer techniques. Theoretical analysis of the latter data has shown that in most cases the clusters which are observed microscopically consist of paracrystalline fragments of known crystalline topologies. The fragments are small (dimensions of order 50 - 100 Å) and the surface/volume ratios are large. As a result the molecular signatures of the cluster surfaces can be identified in the Raman and Mössbauer spectra. Examples will be discussed for g - SiO_2 , g - GeO_2 and chalcogenide alloys over wide and continuous composition ranges.

METALLIC GLASSES

Giessen, B.C.

Northeastern University,
Boston, Massachusetts, U.S.A.

Metallic glasses resemble crystalline metals in their bonding and the basic features of their electronic structure; however, they resemble liquid metals and nonmetallic glasses in that they lack long range periodicity and, accordingly, have many physical properties that differ radically from those of their crystalline counterparts. They can be prepared by rapid quenching of the liquid, often with remarkable ease; compositions that require cooling rates of 10^5 to 10^6 K/sec are designated as readily glass forming; this includes alloys such as $\text{Pd}_{80}\text{Si}_{20}$, $\text{Ca}_{70}\text{Al}_{30}$, $\text{Ni}_{75}\text{Mo}_{17}\text{B}_8$, $\text{Zr}_{50}\text{Cu}_{50}$ and hundreds of other compositions.

In the somewhat over 20 years since the first preparation of a metallic glass by rapid cooling of a molten Au-Si alloy, metallic glasses have been the subject of extensive basic and applied studies. Principal topics of current basic research are their formation, atomic structure and transport, thermal behavior, electronic properties, especially magnetism and electrical resistivity, mechanical properties, especially hardness, ductility and wear and chemical properties, especially corrosion resistance and possible catalytic properties. At present the principal technological applications of metallic glasses are seen as soft magnetic materials in transformers, etc., and as starting material for high-strength devitrified alloys. Other applications are as corrosion resistant coatings, high strength fibers and brazing alloys. Accordingly, major applied research topics are improved fabrication methods, development of specific magnetic and other alloys, thermal stability and strength.

In the context of the present conference it is of special interest to review the thermal properties which include relaxation, single or multiple crystallization steps and, frequently, a glass transition.

POLYMER GLASSES

O'Reilly, J.

Eastman Kodak Co., Rochester, New York, U.S.A.

Glass formation in polymers and in inorganic and metallic materials results from the freezing of certain degrees of freedom over a narrow temperature range. The freezing-in process is affected by intermolecular and intramolecular factors which determine the position of the glass-transition temperature on the absolute temperature scale. Free-volume models, which are widely used, assume that a critical value of free volume occurs at T_g . For polymers, a configurational entropy model has been useful in explaining the effects of molecular weight, copolymer composition, and crosslinking upon T_g . Neither of these models completely describes the effects of polymer structure on T_g . Since neither the volume nor the entropy (or enthalpy) seems to be the controlling parameter, additional critical parameters must be specified. However, difficult computational problems arise when additional terms are included in the expressions for the free energy and the entropy.

The kinetics of glass formation are often more important in practice than the thermodynamics. Moreover, the associated effects of the freeze-in parameters on other physical properties are encountered often. Relaxation processes occur near T_g and persist many tens of degrees below T_g . The relaxation times that govern these processes depend upon temperature and structure (fictive temperature). In addition, a distribution of relaxation times is necessary to describe the processes. The phenomenological description of these processes is reviewed, and representative values of these parameters are compared for different glasses. Changes in physical properties that are important in the applications of glasses are controlled by these relaxation parameters. Effects of relaxation on other physical properties such as mechanical and electrical are discussed. Although current thermodynamic and kinetic treatments of glass-transition phenomena account for many observations, several improvements are needed.

SEMICONDUCTING GLASSES: FROM SELENIUM TO SILICON

Mort, J.

Xerox Corporation, Webster, New York, U.S.A.

Amorphous semiconducting materials range from photoconducting glasses such as the chalcogenides, a-Se, a-As₂Se₃, to amorphous tetrahedrally-bonded solids such as a-Si. While not strictly glasses the latter have important similarities and differences to the chalcogenides. In both cases these materials have demonstrated potential technological importance ranging from electrophotography to thin film, low cost, solar photovoltaic cells. In combination with these practical applications an understanding of the fundamental properties of these disordered materials constitutes a major challenge and activity in the field of solid state physics. A comparative review of the photoelectronic properties of these different classes of amorphous materials will therefore be given and used to account for the actual or potential applicability in particular technologies.

SESSION III

MELTING OF GLASS

PROGRESS IN ELECTRIC MELTING OF GLASS

Staněk, J.

Institute of Chemical Technology,
Praha, Czechoslovakia

The interest in electric melting of glass and its use have increased substantially during the last ten years. This is due not only to the world energy situation but also because of the fact that during this period much theoretical as well as practical work on electric melting has been done and many outstanding results have been achieved.

A review of latest achievements in electric melting of glass is given. New information concerning the electric, power and temperature fields and their influence on the velocity of the flow of glass in an electric furnace has been obtained.

Progress in physical, mathematical as well as in modelling by means of a leading paper will be shown.

The protection against corrosion of the electrodes as well as their optimal connections with the multiphase sources of power will be described.

The methods of improving efficiency of the electric furnaces and their power and temperature control will be dealt with.

Some new ways how to use electricity for melting glass more efficiently and the economy of electric melting of glass will be discussed.

BATCH MELTING OF HIGH PURITY OPTICAL GLASSES BY LOW FREQUENCY INDUCTION AND THERMAL FURNACE: A COMPARISON

Gombert, J., Gauthier, F.,

Central Research Laboratory, Thomson-CSF, Orsay, France

Two different means of preparation of high purity optical glass batches (range : 100 to 500-grams) have been developed in our laboratory:

- a classical thermal furnace with resistance heating;
- a low frequency induction generator directly heating a platinum crucible.

These melting processes have been compared in terms of glass purity and homogeneity, and energy needs. The effects of the crucible composition on the glass purity have been investigated. Both processes were used to prepare optical glasses of the $\text{Na}_2\text{O} - \text{B}_2\text{O}_3 - \text{GeO}_2 - \text{SiO}_2$ system, as base glasses of an optical fiber fabrication process : the "P.S.L. Technique (Phase Separation and Leaching) (1-2-3).

The first method developed in the laboratory was using a 2-kW thermal furnace with kanthal resistance heating allowing temperatures up to 1290°C . Raw materials were dry powders of oxide components.

A platinum/10 percent - rhodium alloy crucible was used to melt and fine 100 to 500-grams batches.

The second method has been developed to improve the control of the process. A low frequency (7 to 12 kHz) 12-kW induction generator was employed, using pure platinum or platinum alloy as container and susceptor for direct heating.

A good coupling efficiency was achieved and a power of 1 kW (@ 1450°C) was necessary to melt the batch.

To melt optical glasses in a very clean atmosphere and to achieve a very low thermal inertia of the furnace that enables rapid quenching for phase separation control purposes, a cell under gas flow was designed. Exhausted vapors were treated before being rejected in the atmosphere.

The fining was made either in the induction furnace cell or in a classical electrical chamber furnace.

A melting cycle, starting with wet raw materials was optimized in terms of furnace atmosphere purity, and glass homogeneity and reproducibility.

Optical properties obtained on graded index fibers drawn from P.S.L. preforms processed with the base glasses obtained by both methods were identical. This result demonstrates that the low frequency induction heating using a pure platinum crucible is suitable for melting high purity glasses.

Some advantages of the induction method over the thermal furnace are:

- easiness to control the atmosphere, its cleanliness and the filtering of rejected vapors;
- high accessibility of the crucible, allowing a simple control of the process;
- fast melting of the glass, enhanced by strong convective currents, and by the higher temperatures reached (1500°C);
- low thermal inertia, leading to controlled quenching conditions necessary to keep phase separation initiation under control in the process involved.

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THE THEORETICAL LIMITS OF GLASS MELTING PRACTICE

Turner, W.H.

PPG Industries Inc., Spring Church, Pennsylvania, U.S.A.

The ultimate efficiency limits for a practical fuel fired melter are derived from first principles, where possible, and applied to the individual processes which must be combined into any melter.

These limits fall into two categories:

I Total Energy requirements

Batch melting enthalpy depends on the temperature range over which heat capacity must be integrated, and the composition and amount of any volatiles. Since all oxides have similar heat capacities, the composition of the glass has only a small effect.

Structure losses are related to the geometry chosen to satisfy the often conflicting needs for maximum flame coverage, combustion volume, and residence time and pull rate, along with minimum outside surface area and heat conduction through the walls.

Combustion product sensible heats represent a large loss even under optimum conditions, since no heat recovery scheme will approach 100% efficiency.

Forming losses are largely unrecoverable, since the enthalpy lost in cooling the glass in forming is not in a form suitable for heat exchanging.

II Rate Processes

The generation of heat and transfer to the walls, crown, and glass is the primary rate controlling step in the process. This is limited by emissivity, practical combustion space limitations (and thus residence time) and the relative temperatures of the gas and surroundings.

Mass transfer limits the rate at which hot glass can be removed from the batch melting area to be replaced by cold glass/batch. The physical size of the melter is limited by the requirement for sufficient volume to achieve some minimum residence time to attain adequate glass quality. This in turn places restrictions on tank pull, geometry and structure losses.

Chemical reactions in general go spontaneously as soon as the batch/glass attains a sufficient temperature. Even the slowest reactions involving silica appear to be much faster than the practical rate of heat input. These are not, in general, rate limiting steps in glass melting.

Summary

Based on numerical examples associated with the above limiting cases, it appears that heat transfer into the glass, and mass transfer within the glass, are the primary factors governing the efficiency of melting with fossil fuel.

COMPOSITION AND OPERATIONAL CONSIDERATIONS IN THE ALL-ELECTRIC MELTING OF AMBER GLASS

Word, W., Cox, H.S., Foley, P.P.

Coors Container Company, Golden, Colorado, U.S.A.

The all-electric melting of amber container glass affords some unique and challenging problems. During early 1979 the Glass Division of Coors Container Company initiated operation on its 150 ton all-electric melter. The initial production of the tank was plagued with unstable amber glass. Problems manifested themselves in terms of conventional color control with excessive blisters and seeds.

As an example, carbon as a conventional means for minor color adjustments proved unworkable as increases or decreases in this component showed no impact on color control or blistering. Similar lack of response occurred with adjustments in iron pyrite, the iron supplement initially utilized in this formula. Compounding the problem was the fact that color requirements for containers produced off this furnace were extremely dark. Light transmission at 550 nm corrected to 1/8 inch was required to be 10-14%. It was only when the ratio of iron and sulfide was considered that control of color and stability of glass in terms of reduced blistering was achieved. This was necessary due to the electric furnace's unique ability to retain sulphur at significantly higher rates than conventional furnaces. In addition to this batch formula change, it was necessary to distribute power input in such a manner that the major input occurred at the charging end. Conditions toward the throat required conversion to a warm top, loose batch condition. These furnace adjustments created the appropriate time/temperature condition for reduction in seeds from entrapped air and CO₂ generation from the fusion process. Once stabilized, this furnace has provided a very stable high quality amber glass whose properties are very suitable for consistent, high speed container operation. Other areas discussed include oxidation/reduction parameters for electrically melted amber, cullet percentages and pull rate adjustments in maintaining stable glass conditions.

FIBREGLASS DRAWING TECHNIQUE OF LOW-MELTING GLASS
MELTED BY NATURAL GAS IN CRUCIBLE EQUIPPED WITH NON-
PLATINUM NOZZLE PLATE

Li Zhi-min, Shanghai Building Materials Institute and
Shi Qion-hua, Chongqing Tugiao Fibreglass Plant,
Sichuan Province, China

Up to now, there are two ways to produce fibreglass, namely, the Tank furnace method and the Crucible method. The former is suited for production on a large scale. The latter uses comparatively simple equipment and its production scale can be arranged at will. However, the method is highly energy inefficient and consumes the electrodes of the noble metal. Some districts in China were incapable of supplying the abundance of power needed, but they are rich in cheap fuel resources, such as natural gas, liquified petroleum gas, coke-oven gas and others. The idea of using local raw materials and resources naturally led to the development of medium and small sized fibreglass factories at the district level.

Since 1976, we have used white sand stone, a natural stone shaped easily, as refractory and liquified petroleum gas or natural gas as fuel, and adopted short-flame combustion, instead of electrodes. We have been successful in applying the platinum nozzle plate crucible and the nickle alloy nozzle plate crucible. We carried out a great number of tests on glass marbles with a medium alkali content and high alkali glass. The results of these tests were satisfactory. They indicated that the simple flame combustion crucible can be utilized to produce fibreglass. The simplicity of the equipment and technique is a definite advantage when compared with the electric furnace. Also, the crucible technique only requires about one third of the power of an electric furnace which leads to a cost saving of about 30%. Furthermore, the crucible can be used continuously over a six month period. The temperature of the surface of the molten glass is 1320°C - 1340°C , in agreement with the calculations. The temperature of the nickle alloy bushing is 1050°C - 1070°C , and the level of the molten glass is about 220 (mm). The diameter of fibre produced is 7~8 micron.

APPLICATION OF RARE EARTH COMPOUNDS IN THE MANUFACTURE OF GLASS

Kibbe, M.R., Molycorp Inc.
White Plains, New York, U.S.A.
and Bauer, W.C., Colorado School
of Mines, Golden, Colorado, U.S.A.

The rare earths, a family of elements with atomic numbers 57 to 71, tend to occur together in several different minerals in nature. Because of their close similarity in atomic structure, they were difficult to separate. Within the last twenty to thirty years, new processing techniques and the development of large mineral deposits have raised the so-called "rare earth" elements from obscurity to readily available commercial status. In fact, the abundance of these elements is rapidly leading to the use of a more sensible definition as the "lanthanides", elements 57 to 71.

Consequently, much research has been undertaken to develop new applications in the field of ceramics. In the specific area of glass technology, certain lanthanides are now used for the decolorizing of flint glass, the prevention of browning in glasses subject to radiation, lasers, and optical glasses with high index of refraction and low dispersion.

The possible use of certain lanthanides as a replacement for arsenic oxides and various sulfates as melting and homogenizing aids in the manufacture of commercial glasses has also received much attention. In general, positive results have been obtained.

Molycorp, Inc., a wholly-owned subsidiary of Union Oil of California, produces the lanthanide chemicals from an extensive deposit of mineral bastnasite located in California. In conjunction with the Colorado School of Mines Research Institute an extensive research project has been initiated to define the potential of the lanthanides as melting and homogenizing aids in the manufacture of glass.

Based upon the results from several laboratory procedures, mainly crucible melts and hot stage microscope work, beneficial enhancement of glass melting has been obtained. Accelerated dissolution rates for silica have been observed at melting temperatures as low as 2250⁰F (1230⁰C) without the additive itself becoming a source of bubbles in the glass as is often the case when arsenic oxide and various sulfates are used.

The basic bastnasite mineral has been found as effective as the various individual "lanthanides" refined from it. Bastnasite concentrations in the range of 0.5-1% by weight in the batch have been found to be essentially equivalent as a melting aid to the normal sulfate additions now routinely employed in the melting of glass batch at normal furnace temperatures. At somewhat lower than normal temperatures, however, the bastnasite maintains a greater activity as a melting aid than that of a reduced flint (carbon-salt cake) batch. The reduced energy requirements which would result from lower operating temperatures present an attractive alternative for the use of the bastnasite.

Continued experimental investigations are planned to develop the operating information required for a complete economic evaluation on the use of bastnasite as a melting aid.

A LABORATORY STUDY OF GAS BUBBLE CHEMISTRY IN MOLTEN GLASS

Lingscheit, J.N. , Malani, N., Smith II, J.S., Ford Motor Company
Dearbourne, Michigan, U.S.A.

Begley, E.R., Davis, A.D., Jackson, F.D.
Corhart Refractories, Louisville, Kentucky, U.S.A.

Gas bubbles are a normal by-product of the decomposition and melting of glass batch; however, the persistence of those bubbles for a period of time sufficient to be trapped in the solidifying glass product is not normal. Gas bubbles are a particularly troublesome defect, periodically imposing heavy yield penalties on a float glass operation. Bubble defects do not normally disrupt the operation of a float glass tank, and their persistence is too often symptomatic of an upset condition.

The industry-wide approach to the sourcing of bubble defects is to sample representative defects, analyze (by mass spectrometry or gas chromatography) the gaseous contents of the bubble, and use the resulting chemical information (and a previously accrued inventory of experience) to deduce the cause of the bubble defect. This approach has been unsatisfactory, resulting in confusing data and misleading interpretations, due in large part to the change with time of the chemical composition of gases in a bubble entrained in molten glass. The goal of this experimental program is to systematically generate an understanding of how bubble compositions change with time and temperature in molten glass. Armed with this understanding, an orderly evaluation of production defects may then be undertaken, progressing toward the deductive sourcing of gas bubble defects.

To achieve this goal, a laboratory technique and attendant equipment have been developed to investigate the chemical changes which take place in a gas bubble in molten glass. Bubbles of known gas composition are created in the float glass by diamond drilling a depression into one of two mating glass wafers. After cleaning, the two wafers are sealed by heating while

immersed in an atmosphere of the desired bubble composition. Having generated a bubble of known gas composition in production float glass, the next task is to promote a reaction between the bubble and the host glass matrix. This is accomplished by exposing the sample to a controlled time-temperature condition, while containing the sample in such a manner as to insure that the gas bubble remains in the glass.

Conventional, resistance furnacing with programmable control serves as a heat source for the treatment of the bubble specimens. A crucible assembly was designed and fabricated from fused silica to hold the cylindrical bubble-glass specimens and to permit visual observation during the entire experimental cycle. Because the sample is heated to temperatures at which the glass is molten, the entire crucible assembly must be rotated during the experiment to prevent the buoyant escape of the bubble. After the programmed temperature-time cycle is complete, the sample is retrieved from the crucible; and the residual gaseous contents of the bubble are analyzed by mass spectrometry.

Preliminary experiments have proven the feasibility of this approach, as molten samples have been successfully retrieved, annealed, and analyzed. Our initial work indicates that the composition of air bubbles in clear glass changes with time and temperature. Some preliminary results of heat-treated nitrogen, carbon dioxide, and oxygen bubbles in clear glass will also be presented.

DIFFERENTIAL THERMAL ANALYSIS OF GLASS BATCHES
CONTAINING SODIUM SULFATE AND CARBON

Taylor, T.D., and Rowan, K.

Clemson University, Clemson, South Carolina, U.S.A.

Considerable work regarding the interaction of glass batches together with minor amounts of sulfate containing and carbonaceous materials has been done. Techniques such as hot stage microscopy and melting rate studies were employed. Some work has also been undertaken to study the reactions of sulfate materials with glass batches using Differential Thermal Analysis, (DTA), but to date, few have utilized this technique to study those glass batch reactions which occur when both carbon and sulfate containing materials are present, yet these latter conditions have been utilized commercially to accelerate the melting of glass. This project was instituted to discover the causes of this accelerated melting. This paper is concerned with those reactions which have been observed during the course of this investigation.

Measurements were first made using only the pure components, so as to be able to identify component transformations in later more complex experiments. Experiments were then carried out with samples containing two components in molar ratios identical to those of the final batch ($0.2 \text{ Na}_2\text{SO}_4 \cdot 0.8 \text{ Na}_2\text{CO}_3 \cdot \text{CaO} \cdot 5 \text{ SiO}_2$). Similar studies were carried out for three components and finally four components.

As a result, most of the features found in the complete batch were identifiable.

ELECTRIC MELTING OF GLASS

Reynolds, M.C.

KTG, Leigh-on-Sea, Essex, England

The general principles of electric melting of glass are covered briefly, special reference being made to the effect of glass composition on furnace design and operation. In particular, the effect of alkali content on glass resistivity is shown and the need to carefully evaluate this is stressed.

Slides and films of convection currents arising from various arrangements of electrodes will be shown and comparisons made between vertical and horizontal systems.

The effect of conductive refractory walls and bottoms on the electric current paths in the tank is shown by use of special model techniques, this being especially important in the melting of high resistivity glasses.

The evolution of various furnace designs is discussed and the wide range of electric furnaces from less than 1 ton/day to over 250 tons/day is shown.

Various power supply systems are illustrated, including the use of SCR control, etc.

SESSION IV

STRUCTURE AND PROPERTIES OF GLASS

BEHAVIOUR OF FLUORINE IN GLASS MELTS

Scholze, H.

Fraunhofer-Institut für Silicatforschung
Würzburg, Federal Republic of Germany

Fluorine is a relatively abundant element and is therefore present in all glasses. The effect in a glass melt can be favourable but also less favourable.

Since the classical studies of V.M. Goldschmidt it is known that there are glasses that contain fluoride as the sole anion. BeF_2 - glass is a weaker version of the SiO_2 - glasses. The formation of fluoride glasses is also promoted by AlF_3 or ZrF_4 . In all probability the simultaneous presence of different configurations $\{\text{MeFx}\}$ plays an important role in glass formation.

Fluorine glasses display excellent IR-transmission. However, a strong band assigned to OH groups can often be observed at 2.73 μm . The shape of the band is similar to the corresponding band in SiO_2 glass. The water content of silicate glasses is decreased in the presence of fluoride. On the other hand the presence of water reduces the fluoride content of glasses.

The interaction between fluoride and water content in a glass can be explained in terms of the thermodynamics of the system. The presence of fluorosilicates of the general form $[\text{SiO}_{4-n}\text{F}_n]^{4-n}$ has to be taken into account when considering melts of the anhydrous $\text{NaF-Na}_2\text{O-SiO}_2$ system. The result is dissociation of Si-O-Si bonds and a lowering of the viscosity.

This process forms the basis for the action of fluorine in accelerating the melting process, and also at least in part for its action as a

fining and nucleating agent. When $n=4$, gaseous SiF_4 is formed which vaporizes. In the presence of water the usual stable (volatile) component is HF.

The proportion of fluorine that is lost from the glass melt through evaporation is not only dependent on the water content of the furnace atmosphere but above all on the fluorine content of the melt while the nature of the raw materials plays a secondary role. Most of the fluorine escapes during the initial phase of the melting process. The total emission during the entire melting process is not very large. Usually it is in the order of 30% of the initial fluorine content (which is on the average about 0.04 wt% of fluorine).

VISCOSITIES OF IRON-CONTAINING SILICATES IN THE ANNEALING RANGE

Fasano, B.V. and Klein, L.C.

Rutgers - The State University of
New Jersey, Piscataway, New Jersey,
U.S.A.

Viscosities in the range 10^8 to 10^{14} poise were measured for glasses in the $\text{FeO}_x\text{-Na}_2\text{O-SiO}_2$, $\text{Al}_2\text{O}_3\text{-Na}_2\text{O-SiO}_2$ and $\text{FeO}_x\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-SiO}_2$ systems. The compositions contained approximately 2, 5, 10 and 20 mole pct of all FeO_x , all Al_2O_3 or half FeO_x and half Al_2O_3 . All of the glasses had 20 mole pct Na_2O . These viscosities correspond to the temperature range from about 400°C to 750°C.

Comparisons were made between glasses prepared in air with Fe_2O_3 and glasses prepared in forming gas (95% N_2 - 5% H_2) with Fe_3O_4 or with enough carbon to reduce Fe_3O_4 to FeO . The glasses prepared under oxidizing conditions had Fe^{2+}/Fe total ratios less than 0.25 and the glasses prepared under reducing conditions had Fe^{2+}/Fe total ratios greater than 0.25, with the glasses prepared with carbon having Fe^{2+}/Fe total ratios greater than 0.50. Viscosities were determined in a beam-bending viscometer with controlled atmospheres, and the Fe^{2+}/Fe total ratios were determined by $\text{K}_2\text{Cr}_2\text{O}_7$ titration.

In general, the viscosity at a given temperature decreased with increasing FeO_x in the $\text{FeO}_x\text{-Na}_2\text{O-SiO}_2$ system, increased with increasing Al_2O_3 in the $\text{Al}_2\text{O}_3\text{-Na}_2\text{O-SiO}_2$ system and increased with increasing $(\text{FeO}_x + \text{Al}_2\text{O}_3)$ in the four-component system. For a given $\text{Na}_2\text{O-SiO}_2$, the glass with FeO_x had the lowest viscosity and the glass with Al_2O_3 had the highest viscosity, while the glass with equimolar $(\text{FeO}_x + \text{Al}_2\text{O}_3)$ had an intermediate viscosity. In general, the glasses prepared under oxidizing conditions had higher viscosities than glasses prepared under reducing conditions, with or without carbon. The viscosity-temperature relation for the Fe-containing glasses showed curvature but the relation for glasses in the $\text{Al}_2\text{O}_3\text{-Na}_2\text{O-SiO}_2$ system were nearly straight.

When a Vogel-Fulcher relation was used to fit the data, with $T_g (= 10^{13}$ poise) as a corresponding states parameter, it was found that the data could be fit with three curves, one for each oxidation condition. The effects of composition and oxidation condition on the flow behavior of slags which tend to be oxidized and the flow behavior of terrestrial magmas which tend to be reduced have been considered.

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MAGNETIC PROPERTIES OF SOME LEAD BORATE GLASSES WITH TRANSITION METAL IONS

Ardelean, I., Ilonca, Gh., Cozar, O.

Babes-Bolyai University,
Cluj-Napoca, Romania

Several experimental results suggest that the valence states and distribution mode of the transition-metal (TM) ions in the network of the oxide glasses depend on the structure of the glass matrix (1), preparation conditions (2) and the nature of the TM ions (3).

In order to extend the available information on these problems, we have studied the structure and magnetic properties of some lead borate glasses with various amounts of CuO , V_2O_5 , MnO , CoO , NiO , CuO.MnO and $\text{CuO.V}_2\text{O}_5$, using X-ray diffraction analysis, EPR and magnetic susceptibility measurements. All samples were prepared under the same conditions (the melting has been realised, in sintered corundum crucibles at the equilibration temperature $T_M = 1150^\circ\text{C}$, for 1 h) using the same glass matrix ($2\text{B}_2\text{O}_3.\text{PbO}$). The concentrations of the samples have been evaluated using the formula $x\text{MO}.(1-x)(2\text{B}_2\text{O}_3.\text{PbO})$, where MO represent the above enumerated TM oxides.

The X-ray diffraction analysis showed that the range where prepared glasses are homogeneous depends on the nature of TM ions. Thus, the higher concentrations up to which the homogeneous glasses form lie between $x = 80 \text{ mol } \%$ (for MnO) and $40 \text{ mol } \%$ (for NiO).

From magnetic susceptibility and EPR studies (EPR measurements have been made for the glasses with CuO , V_2O_5 , MnO , $\text{CuO.V}_2\text{O}_5$, CuO.MnO) was determined the concentration range where the TM ions are magnetically isolated and where these ions participate at the magnetic superexchange interactions. The values of the maximum concentrations of the TM ions where these are isolated are presented in Table 1.

Table 1.

MO	CuO	MnO	CoO	NiO	V ₂ O ₅	CuO.MnO	CuO.V ₂ O ₅
(mol % MO)	5	30	50	50	55	< 5	20

The cobalt, nickel and vanadium ions are magnetically isolated within the whole concentration range of these glasses. On the other hand the copper, manganese, copper-manganese and copper-vanadium ions are isolated in a limited concentration range. At higher concentrations, the temperature dependence of the reciprocal magnetic susceptibility obeys a Curie-Weiss law with negative paramagnetic Curie temperatures. Also, for these concentrations the resonance linewidth increases not proportionally to the concentration. These data indicate that the TM ions in the glasses experience negative exchange interactions and are coupled antiferromagnetically. In this case, the antiferromagnetic order takes place only at short-range, and the magnetic behavior of glasses can be described by the so-called mictomagnetic(4) or speromagnetic (5) type order.

From the comparison of the experimental and calculated values of the Curie constants it was concluded that the TM ions are in the following valence states: $\text{Cu}^+-\text{Cu}^{2+}$, $\text{V}^{4+}-\text{V}^{5+}$, $\text{Mn}^{2+}-\text{Mn}^{3+}$, Co^{2+} , Ni^{2+} and in the mixed TM ions glasses the valence states found for the single type TM ions glasses coexist. These data also permitted to determine the molar fraction of the TM ions in the different valence states, taking into account the atomic magnetic moments in the free ion states. Taking into consideration higher values of the paramagnetic Curie temperatures (in the case of mixed TM ion glasses comparatively to the simple TM ion glasses), which are proportional to the number of TM ions participating at the magnetic interaction, we have concluded that in the case of the mixed TM ion glasses the simple ion pairs $\text{Cu}^{2+}-\text{Cu}^{2+}$, $\text{V}^{4+}-\text{V}^{4+}$, $\text{Mn}^{2+}-\text{Mn}^{2+}$, $\text{Mn}^{3+}-\text{Mn}^{3+}$ coexist with the mixed ion pairs $\text{Cu}^{2+}-\text{Mn}^{2+}$, $\text{Cu}^{2+}-\text{Mn}^{3+}$, $\text{Mn}^{2+}-\text{Mn}^{3+}$. This last result is also confirmed by the EPR spectra, being in agreement with similar data obtained for other oxide glasses with TM ions (6).

In the case of the copper, manganese and vanadium ions, from the concentration evolution of the EPR spectra, we have evaluated the ratio between isolated and clustered species of TM ions.

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FINE STRUCTURE OF THE SURFACE LAYER OF BIOGLASS AND SINTERED HYDROXYAPATITE

Fujiu, T., Ogino, M., Kariya, M., Ichimura, T.

Nippon Kogaku, K.K., Kanagawa,
Japan

Bioglass and sintered hydroxyapatite (SHAP) have been known as typical biomaterials that can create direct bonds between bone and themselves. A general explanation for the bonding mechanism is that these two materials have a similar apatite structure on the surface as bone has. However, the surface layer formed on bioglass was only found to have a basic apatite structure composed of Ca^{2+} and PO_4^{3-} that have a 6-fold axis by IRRS, and there was no information about the anion on the symmetry axis. On the other hand, there was some information about this anion in SHAP by IRAS and ESR, but the change that may occur on the surface after implantation was not studied yet. In the present study, fine structure of the surface layer on two types of bioglass and SHAP were examined after in vitro treatment by IRAS and NMR to know variation and content of the anion. Then, in vivo experiments were employed to try to study the relation between bonding strength and fine structure of the surface layer of these three materials.

The materials used were bioglass 52S4.6, bioglass 52S4.6F $\frac{1}{2}$ (half the amount of CaO was substituted by CaF_2 in the 52S4.6 composition), SHAP and canine femur as a standard of comparison.

1. In vitro experiments.

Two types of bioglass and SHAP were exposed to a simulated physiological solution (37°C, pH7.4), and the resulting reaction layers were removed to be examined by IRAS and NMR. One part of this removed layer was deuterized in 50°C D_2O before the examination by IRAS to identify OH^- ions on the symmetry axis. The bone mineral was examined in the same way.

2. In vivo experiment.

These three materials were processed into a cone shape and followed by implantation in rabbit femur. The bonding strength between bone and these materials was measured four weeks after implantation.

From the in vitro experiment it was shown that the surface layers of these three materials having the same basic apatite structure were different in regard to the anion on the symmetry axis. In the surface layer on bioglass 52S4.6, some amount of OH^- ions were substituted by CO_3^{2-} ions. And the surface layer on bioglass 52S4.6F $\frac{1}{2}$ contained F^- ion as most dominant anion on the symmetry axis. This certifies the formation of fluoroapatite. Furthermore, since the surface layer on SHAP had the same apatite structure as in the bulk, it is suggested that the most dominant anions on the axis are O^{2-} and O_2^{2-} . As bone was found to have the CO_3^{2-} ion substituted for the OH^- ion, it is concluded that the fine structure of the bioglass 52S4.6 surface layer is most similar to that of bone. In vivo experiment showed that the region where fracture occurred under loading condition depended on the material. In the case of SHAP the fracture occurred between bone and the surface layer and in the case of bioglass 52S4.6, between the surface layer and bulk glass. Therefore, careful attention must be paid to the fracture region in discussing bonding strength between bone and these biomaterials.

THE MIXED ALKALI EFFECT IN LITHIUM-SODIUM BORATE GLASSES*

Jain, H.^a, Brookhaven National Laboratory, Upton, New York, U.S.A.

Downing⁶, H.L. and Peterson, N.L.
Argonne National Laboratory, Argonne, Illinois, U.S.A.

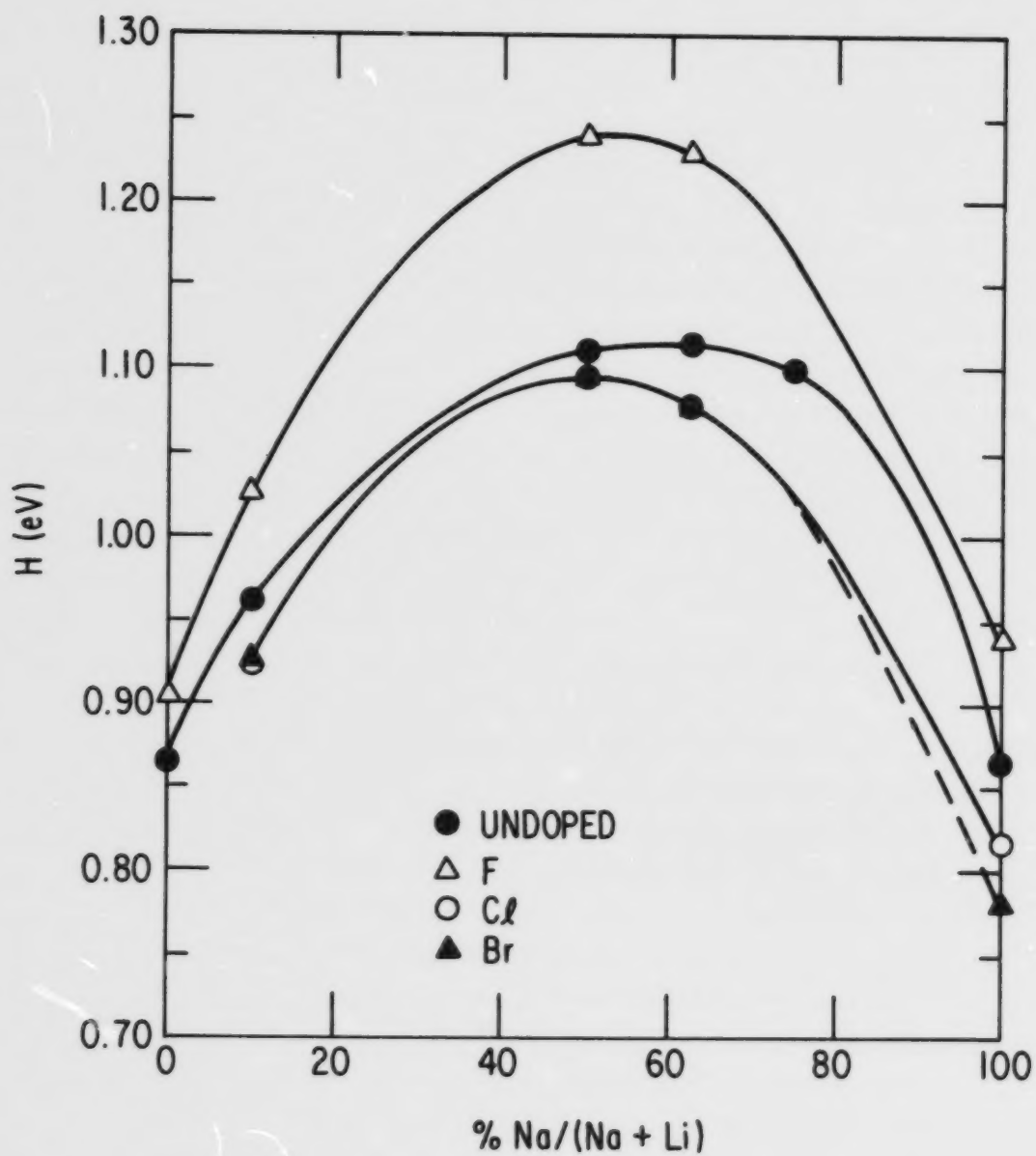
To understand the mixed alkali effect in glasses, we have investigated the electrical conductivity of $(\text{Li,Na})_2\text{O}:2.86 \text{ B}_2\text{O}_3$ glass series with the fraction $\text{Na}/(\text{Na}+\text{Li})=0, 0.1, 0.5, 0.625, 0.75$ and 1.0 . A.c. conductance and capacitance were measured in the temperature range of $150-350^\circ\text{C}$. The bulk conductivity at each temperature was obtained using complex impedance analysis and then least square fitted to an Arrhenius type equation. The conductivity shows a strong minimum at $\text{Na}/(\text{Na}+\text{Li}) \sim 0.6$, which becomes more pronounced as the temperature is decreased. The origin of this minimum may be found in the activation enthalpy (H) which shows a maximum at the same composition.

To determine the role of a negative ion on the mixed alkali effect, the glasses were doped with halogens and, its effect on conductivity was measured. To keep the same basic structure, only about 1% of total oxygen was replaced by fluorine, chlorine or bromine; the alkali concentration was kept constant. In general, relative to an undoped glass the electrical conductivity increases by doping with chlorine or bromine. An opposite effect is found for fluorine doping. The mixed alkali effect, as shown in the figure in terms of compositional dependence of activation enthalpy, is enhanced by the addition of fluorine, but is slightly diminished by chlorine or bromine. These observations may be interpreted in terms of the mechanism by which a halogen is incorporated in the glass structure viz. fluorine enters covalently as a part of glass forming network, whereas chlorine or bromine is considered to be interstitially 'dissolved'.

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^a Part of the work was carried out at Argonne National Laboratory

⁶ Present address: Physics Department, Drake University, Des Moines, Iowa 50311



GERMANIA CONTAINING GLASSES WITH POTENTIAL FOR INFRARED WAVEGUIDES

Nassau, K., and Chadwick, D.L.

Bell Laboratories, Murray Hill, New Jersey, U.S.A.

Using a previously described approach to calculate the optical dispersion parameters, (K. Nassau, Bell Syst. Tech. J. 60, 327, 1981; K. Nassau and S. H. Wemple, Electronic Letters, in press) it is possible to predict that glasses based on GeO_2 or As_2O_3 in combination with heavy metal oxides such as PbO , Te_2O , Bi_2O_3 and/or Sb_2O_3 could have properties suitable for optical waveguides in the 3 to 4 μm region. For a large bandwidth, so that long lengths of low loss fiber can be utilized, it is necessary to balance the negative material dispersion parameter $M = -(\lambda/c)(d^2n/d\lambda^2)$, where c being the velocity of light and n is the refractive index at wavelength λ , against the waveguide dispersion as determined by the waveguide design parameters.

One of the parameters which can be calculated is the value of λ_0 , the wavelength where the material dispersion parameter becomes zero; this is calculated to be 3 to 3½ μm for these compositions. The dispersion slope $dM/d\lambda$ is calculated to be about half the -100 psec/nm.km. μm of fused silica, so that balancing of this against the positive waveguide dispersion should permit high bandwidth operation in the infrared well beyond λ_0 .

The six pseudo-ternary phase diagrams of GeO_2 with all combinations of two oxides from the list PbO , Te_2O , Bi_2O_3 , and Sb_2O_3 were examined by melting and air cooling or water quenching samples in platinum crucibles in air. Wide areas of glass formation were found in all but the GeO_2 - Te_2O - Sb_2O_3 system.

Examples of compositions which gave bulk glass by merely aircooling 25 g specimens in heavy walled platinum crucibles include (expressed in cation percent)

19 GeO_2 : 37 $\text{BiO}_{1.5}$: 44 $\text{TeO}_{0.5}$,
41 GeO_2 : 20 PbO : 39 $\text{TeO}_{0.5}$,
34 GeO_2 : 33 $\text{BiO}_{1.5}$: 33 PbO ,
22 GeO_2 : 22 PbO : 56 $\text{SbO}_{1.5}$, and
27 GeO_2 : 36 $\text{BiO}_{1.5}$: 37 $\text{SbO}_{1.5}$.

Several four and five component compositions also yielded glass, including

40 GeO_2 : 20 $\text{SbO}_{1.5}$: 20 $\text{BiO}_{1.5}$: 20 PbO .

Typical properties can be illustrated for the four-component glass composition listed above, which had a glass transition temperature of 400°C , a crystallization temperature of 480°C , and melted at about 750°C . Its density was 6.27 g.cm^{-3} and the thermal expansion coefficient was $11.5 \times 10^{-6} \text{ K}^{-1}$.

Merely dipping a platinum wire into such melts and withdrawing slowly permits meter lengths of fibers to be drawn. Preliminary optical dispersion measurements confirm the expected λ_0 and $dM/d\lambda$ values.

SPECTRA OF Eu^{+3} ACTIVATED FLUORESCENCE IN RELATION TO THE STRUCTURE OF BOROSILICATE GLASSES

Hall, M.R.

Southern Illinois University, Carbondale, Illinois, U.S.A.

Excitation, absorption and fluorescence spectra were measured for Eu^{3+} -activated borate and borosilicate glasses which contained the divalent modifiers Mg, Ca, Sr or Ba. Systematic changes in the spectra are related to the kind of modifier site in which the Eu^{3+} ion locates and to change in the host glass structure. The Eu^{3+} ion interchanges positions with the major modifier cations when the temperature is above the glass transition temperature and below this temperature tends to be frozen into sites of a size determined by the size of the modifier cation. The field strength of modifier ions, particularly at concentrations above 30 mol %, affects the oxygen polarization around the Eu^{3+} site. These conditions are systematically correlated with changes in the intensity of luminescence, the thermal quenching of luminescence, wavelength shifts, 'crystal'-field splitting of energy levels, and inhomogeneous spectral broadening. The thermal history of the glass samples affects the magnitude of the observed spectral changes but does not obscure the trends which relate to the nature of the Eu^{3+} site and the glass composition.

The ratio of intensities for the $(^5\text{D}_0 \rightarrow ^7\text{F}_2)/(^5\text{D}_0 \rightarrow ^7\text{F}_1)$ emissions indicate the magnitude of the noncentrosymmetric component of the electric field at the Eu^{3+} site. This ratio is maximum for compositions such that the fraction of four-coordinated boron is near maximum, and at compositions for which the mol % SiO_2 is nearly equal to the mol % of B_2O_3 . Increasing the fraction of four-coordinated boron correlates with 1) decreasing centrosymmetry of the Eu^{3+} site, 2) increasing Eu-O interaction as indicated by larger 'crystal'-field splitting of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ multiplet, and 3) decreasing uniformity of the Eu^{3+} sites as indicated by greater inhomogeneous broadening of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ emission. Increasing fractions of non-bridging oxygens at higher modifier concentrations correlates with trends which are the reverse of those observed for increasing four-coordinated boron.

These effects can be explained with the aid of a structural model which enumerates bonding states by assigning to the oxygen bonds an energy value determined by the cation type and the coordination of the cation.

PHOSPHATE-VANADATE GLASSES IN THE SYSTEM
 $\text{Ba}(\text{PO}_3)_2\text{-V}_2\text{O}_5\text{-Ag}_2\text{O}$. STRUCTURE AND PROPERTIES

Wasyłak, J., Koprowski, J., Berg - und Hüttenakademie,
Krakow, Poland, and

Czerwosz, E., Forschungs - und Entwicklungszentrum
der Flächenbildröhren,
Warszawa, Poland

If the glass forming region of the $\text{Ba}(\text{PO}_3)_2\text{-V}_2\text{O}_5\text{-Ag}_2\text{O}$ system is determined and the structure and properties are investigated, it can be concluded that the viscosity decreases and rapid undercooling occurs with increasing V_2O_5 content of these glasses. The stability and chemical durability of these glasses improves with increasing $\text{Ba}(\text{PO}_3)_2$ content.

The Raman spectra of glasses in the $\text{Ba}(\text{PO}_3)_2\text{-V}_2\text{O}_5$ system containing between 10 and 20 mol % V_2O_5 shows that metaphosphate ($675, 1146\text{ cm}^{-1}$) and orthophosphate ($965\text{-}975, 1045\text{-}1095\text{ cm}^{-1}$) are present. No Raman spectra could be obtained for glasses containing between 30-50 mol % V_2O_5 because of strong fluorescence.

Raman spectra of glasses with a V_2O_5 content in excess of 60 mol % exhibit the characteristic orthophosphate structure. Bands in the $50\text{-}80\text{ cm}^{-1}$ region can be attributed to vibrations of the V_2O_5 network or its fragments. The spectrum of the vitreous $\text{Ba}(\text{PO}_3)_2\text{-Ag}_2\text{O}$ system (10 mol % Ag_2O) is similar to that of barium metaphosphate ($336\text{-}686, 1003, 1154, 1243\text{ cm}^{-1}$). The glasses with a Ag_2O content in excess of 10 mol % show strong fluorescence.

An analysis of the dependence of the glass properties (d, α, T_g) on glass composition shows that there is a close relationship with changes that occur in the glass structure.

The results of electrical property measurements indicate that the glasses of this system are semi-conductors in the temperature range investigated ($20\text{-}300^\circ\text{C}$). The semi-conducting properties find their origin

in the hopping mechanism of the small polarones between the vanadium ions in the phosphate-vanadate glasses.

A considerable increase in σ_0 and conductivity of the glasses containing 50 mol % of V_2O_5 is indicative of the formation of increasing amounts of vanadium in ($V^{4+}-O-V^{5+}$) in the glass network structure.

For glasses with an increased Ag_2O content, the results show that already at a concentration of 20 mol % Ag_2O a separation of metallic silver from the glass network, a substantial change in σ_0 (especially when compared to the glass containing 10 mol % of Ag_2O) and an increase in the power factor of the dielectric loss factor occurs.

SESSION V

ENERGY

GLASS AND NUCLEAR WASTES

Sombret, C.

Commissariat à l'Energie Atomique
Site de Marcoule, France

The wastes generated by the operation of the spent fuel processing plants are variable due to the difference in nature, radioactivity level, risks associated with the various nuclides they contain and the characteristics of the medium in which they are found (corrosion aspect, pyrophoricity, etc.). Categories have been established by various organizations or agencies. However, it is impossible to classify some specific wastes because they fall into several categories. Glass has often been considered as a conditioning material to many wastes. It is technically possible to vitrify low level radioactive wastes and this has been seen in some cases (Belgium, and in particular, the U.S.A.), but the economical interest of such a process remains to be verified. On the other hand, it is generally assumed that glass, as a conditioning material, is compatible with particular wastes (ultimately iodine trap or incinerator ashes) and more specifically with the high level radioactive liquid wastes. The advantage of using glass as an ultimate storage material is that a liquid can be converted into a solid with minimal radiation hazard and that only small quantities of final waste need be handled. One megawatt of power generated by a light water reactor station yields only three liters of glass per year.

Other materials, mainly ceramics, have often been advocated as ultimate storage media. All of these nearly-crystalline products have advantages and disadvantages when compared with glass. Whether the aforementioned crystalline materials and the glasses lacked the desirable properties for nuclear waste storage or whether other difficulties played a role as well, it is noteworthy that only one industrial plant for solidification of high level radioactive waste is in operation today. The plant which uses glass as a storage medium has been running since 1978.

GLASS MELTING WITH GAS FROM COAL

Günther, R.

University of Karlsruhe,
Karlsruhe, Federal Republic of Germany

Countries in which the consumption of mineral oil is mainly covered by imports are forced to reduce these imports drastically. The high demand on foreign currency for the expensive oil undermines their economy, the political instability of the Near East makes the supply doubtful and a compensation of fuel import costs by exports is easier to realize with coal-exporting countries than with those exporting oil.

For glass melting, the only real alternatives to oil are gas made from coal and electricity, since the reserves of natural gas are limited.

In a number of coal mining countries, coal gas was the main fuel for glass melting for more than a century. The author has experienced the producer gas era in the industries of steel and glass in the time before 1960.

Besides the low calorific value the main disadvantages of producer gas were its content of vapours of higher hydrocarbons and water, the high temperature and fluctuating composition. These difficulties could be overcome by suitable producer control and cleaning of the gases, but the price was reduced economy. In any case it was unavoidable to preheat the gases to about 1000°C by means of gas regenerators.

With the high standard of modern glass quality constant composition of a fuel gas is indispensable. The modern processes for producing gas from coal are suitable to fulfil this demand. The most advanced gasification processes are discussed with regard to their utilisation for glass making. Size of producers, calorific value and byproducts, simplicity and economy are the main items considered.

SONIC ENERGY AS A MEANS TO REDUCE ENERGY CONSUMPTION DURING GLASS MELTING

Spinosa, E.D., and Ensminger, D.

Batelle Columbus Laboratories,
Columbus, Ohio, U.S.A.

Approximately two-thirds of the energy delivered to the melting and molten glass batch in an industrial melter is used to refine the glass (i.e., remove bubbles). If the bubbles present in the melt can be made to coalesce, then this energy requirement can be reduced. Introduction of sonic energy into the melt can induce such coalescence, thereby reducing energy requirements for refining.

This use of sonic energy to remove bubbles in fluids has been known for some time, and it has been attempted in molten glass. All of this technology has been developed around cavitation as a means for inducing bubble coalescence. When this phenomenon is applied to very viscous fluids, such as molten glass, a large energy input is required. This large energy input is both technically and economically prohibitive. However, other, noncavitating, sonic phenomena are available which require a much smaller energy input to achieve the required coalescence. These phenomena can be easily induced in molten glass so that the required bubble coalescence can be achieved.

This paper will provide a technical review of the noncavitating phenomena and how they induce bubble coalescence. It will also present the results of scale modeling experiments used to demonstrate the occurrence of these phenomena in viscous fluids. The results of large size crucible experiments will be presented and interpreted. Finally, an assessment of the technology's potential use in the glass industry will be discussed.

ELECTRO MELTING OF GLASS -- ENERGY EFFICIENT AND ENVIRONMENTALLY POSITIVE

Hülsenberg, D., and Illig, H.J.

Department of Technology,
Berlin, German Democratic Republic

Under the term VES we describe a process whereby glass is melted using 100% electric energy. The glass itself is the main electric conductor. Energy is applied using water cooled molybdenum electrodes.

The development of the VES process was done by the Technical Institute of Jena Glass. This process uses vertically installed electrodes through the bottom.

Two transformers with phase displacement of 90° deliver the electric energy to the glass melt. The transformers guarantee an equal load distribution to the system and a control of the energy supply. The furnace consists of a melting and working end. At the melting end, batch feeding is continuous and automatically controlled. The temperature over the batch blanket is held between 100 and 300°C. Inside the glass bath, depending on glass composition, temperatures of 1,400 to 1,650°C exist.

Depending on throughput requirements, furnaces with melting areas from 1 square meter to 12 square meters are available.

These furnaces are used in the first place to melt borosilicate and alkali calcium glass. Experimental melts for glasses of different compositions have been successful. The throughput of these all electric furnaces, depending on glass composition, is between two to five times that of a fossil fuel fired furnace.

Controlling the direct release of energy into the glass bath has a positive influence on the melting process.

The elimination of the fossil fuel system for the melting section, with its high heat losses, and the reduction in the melting area have reduced the energy consumption quite considerably. It is remarkable that over a furnace campaign the energy consumption is held constant. Energy intensity can be reduced up to 70%.

The environmental condition in the plant is reduced considerably due to the low heat, dust and noise level of the VES process.

Emission values for CO_2 , CO , SO_2 and NO_x are directly reduced. The solid batch blanket over the melt reduces the volatilization of materials having a low partial pressure like fluorine, borax and lead. Besides the improvement in the environmental conditions, material costs for the above named components are reduced.

The high automated VES process guarantees an easy control of the operation and eliminates heavy physical work.

DISTRIBUTION CHAMBER CONCEPT IN GLASS MELTING

Muschalla, B.

Consumers Glass Company Limited,
Toronto, Ontario, Canada

The past 25 years have seen considerable progress made in the design and operation of glass furnaces.

In the 50's, the non-insulated relatively shallow furnaces with all their problems related to operation and glass workability were predominant.

These furnaces had large refiners separated from the melter by a bridgewall and shadow wall. The refiner size was, generally, about 50% of the size of the melter area. The glass gradients were approximately 25°F per inch for colored glasses and 14°F per inch for flint glasses. Furnace efficiencies were in the 20 to 25% range. Heat losses of the melter sidewall and bottom were about 5,300 B.T.U.'s per square inch per hour. The glass entering the forehearth had temperature variations in excess of 200°F, particularly on colored furnaces. Glass workability problems on the forming machines were numerous.

No physical or chemical property measurements made of good or bad workable glass showed any variation which could explain consistently the difference in the working behaviour of the glass. Good control of the process provided the best operating conditions prevailing during that time. Most emphasis was placed on preventing deviations of glass properties caused by either raw materials, batch house problems, furnace operation or foreign cullet.

Over the years, the demand for productivity and throughput has increased. The customer also demanded improved product quality and lower

prices. The industry responded by going to light weighting and increased machine speed, but ran out of capacity with the existing facilities.

The new generation of furnaces, which emerged in the early 60's, provided the increased capacity needed; and the larger and better insulated forehearth gave us the improvement in the temperature distribution so badly needed to form a good container on the faster running machines.

The new generation of furnaces had many advantages:

1. Increased output per square foot of melting area.
2. Reduced fuel consumption.
3. Increased furnace life.
4. Improved glass quality.

The basic furnace design had not changed. The furnace still had a large semi-round refiner, which was separated from the melter by a bridgwall and shadow wall. Furnace efficiencies ranged from 35 to 40%, mainly due to heavy insulation and batch formula changes. Heat losses through the melter bottom and sidewall were reduced by 70%. Glass gradients were reduced to 12°F per inch for colored glasses and 6°F per inch for flint glasses.

With the improved glass conditions, one could have expected to see a reduction of glass workability problems. While there was a definite decrease in the sensitivity toward compositional changes, workability problems had, by no means, disappeared.

Large tonnage fluctuations are always associated with large temperature fluctuations, which made it impossible to maintain temperature stability in the refiner. Best performance existed on furnaces which were pulled near maximum capacity.

By separating the refiner from the dependency of the melting operation, independent temperature controls become possible. This separated section of the furnace is called the distributor.

Problems with the operation of a distributor system can occur when changes in the operation of a furnace occur during a furnace campaign like the addition of an electric boosting system.

The change to a distributor system will help to improve glass temperature homogeneity and reduce glass workability problems.

THE BH-F ENERGY EFFICIENT FOREHEARTH

Vilk, P.* and Mees, M.**

* BH-F (Engineering) Ltd., London, U.K.

**Gallo Glass Company, Modesto, California, U.S.A.

In August 1981, BHF installed the first four of a new series of forehearths known as the 400 series.

The main features of the 400 series forehearth are monobloc roof construction with longitudinal cooling channel, graded insulation to suit production range and automatic control of cooling air. In the newly designed cooling section, cooling air flows longitudinally along the middle of the forehearth roof, entering at the rear and exhausting the combustion products via a single flue at the front of each cooling zone. Where forced air is required, automatic control is provided. In this way the cooling is concentrated on the middle stream of glass.

Forehearth insulation is selected in various combinations to suit particular production requirements, colour of glass and forehearth entry temperature. Several grades of insulation are available.

The BH-F 400 series design offers substantial fuel savings, improved temperature homogeneity of glass, better glass temperature stability, quicker response to fluctuations in forehearth entry temperature, simpler construction techniques, rapid installation and faster control of responses.

Fuel savings have already been achieved in excess of 45 % compared with fuel consumption on forehearths of conventional design. Significant improvements have also been made with respect to glass temperature homogeneity and cooling air volume. The latter has been reduced to as low as 15% of conventional requirements.

Forehearth design and selection is fully computerized. Any production changes can be immediately evaluated as to their impact on fuel consumption and glass temperature homogeneity.

In this paper a basic description of the BH-F 400 series design forehearth and its benefits will be given, supported by results from existing installations.

INTERNAL AXIAL COOLING OF MOULDS IN CONTAINER GLASS PRODUCTION MACHINES

Seidel, H.G.

H. Heye Glasfabrik Abt. International
Obernkirchen, Federal Republic of Germany

Summary

As container glass production methods have been improved, the limitations of conventional radial mould cooling by air have become apparent. This especially refers to the limited control of heat extraction, to the high energy consumption and to the high noise emission. In a search for new and better methods, cooling by means of axial air flow through bore-holes in the mould has been developed. These holes can be arranged equally spaced around the mould and the air supply can be controlled for sectorial groups of holes so as to obtain improved temperature control.

The total surface area of these bore-holes can be made at least 50% greater than the outside surface area of the mould. In addition, the heat transfer coefficient for turbulent air flow through holes is better than the average coefficient for radial cooling. This results in increased heat extraction.

Due to the optimum relationship between surface area and cross-section of small holes, the quantity of air needed for the same amount of heat extraction decreases by a factor 3 compared with conventional radial cooling.

Noise emission is reduced by reducing the quantity of air and by dividing the flow into a large number of small air streams without deflection after leaving the mould. In addition, the axial exhaust of hot air avoids direct flow towards the operator.

For IS-machines, an air supply system has been designed which includes intermittent valve and sector control valves.

The results of the practical use of this equipment in a 10-section Narrow-Neck-Press-and-Blow - machine were as follows:

The efficiency increased by 1-2 % as a result of better temperature control in the blank mould; the speed was increased by 10 % as a result of increased heat extraction in the blow mould; the energy consumption was decreased for the whole machine by a factor 2. The noise emission is definitely lower than with radial cooling. Differences of 6 db(A) have been found.

DIFFRACTION METHODS TO DETERMINE NODE MODEL PARAMETERS
OF THE REAL GLASS STRUCTURE

Bochyński, Z.

Adam Mickiewicz University of Poznań,
Poznań, Poland

The paper includes theory, outline, description of diffraction X-Ray and electron methods and results of the analysis of the real glass structure, obtained at my laboratory.

In this paper investigation results of the internal structure of sodium-silicate glasses ($\text{SiO}_2\text{-Na}_2\text{O-CaO-MgO-R}_2\text{O}_3$) type, silica glasses $\text{SiO}_2\text{-R}_2\text{O}_3$ and silica gels $\text{SiO}_2\cdot x\text{H}_2\text{O}$ are presented.

Data for the calculation of structure parameters used for the description of the internal structure of complex oxide glasses are obtained. The approximative, spatial node model is described.

This model is very useful for the description of glass structure. The use of the model and the accuracy of determining its parameters are discussed.

By subtraction of adequate radial distribution functions and by successive approximations of the effective molecule, by the addition of successive oxide groups (Na_2O , CaO , MgO), parameters enabling the description of the oxide glass node model are determined.

The aperiodic nodal scheme of the node lattice is presented and described, stressing structure parameters and local ordering in groups reflecting the internal structure of complex oxide glasses.

Moreover, sets of structure elements which correspond to the main components of the glass and which form groups with local ordering,

appearing in complex oxide glasses are mentioned schematically.

The correctness of the used analytical method for components of silica gel (SiO_2 , H_2O) and silica glass (SiO_2) is checked and it is then applied successfully to the system of components of sodium-silicate glasses (SiO_2 , Na_2O , CaO , MgO) and silica glass (SiO_2).

The investigations are completed with surface and internal stresses, optical measurements of hardened and tempered glass plates and with microscopy measurements of local microhardnesses.

In this paper the research techniques used, the results obtained, methodology and possible experimental set-ups are outlined.

Also further research perspectives are presented with the aim to obtain more precise structure parameters in structure measurements.

PREHEATING GLASS BATCH IN A FLUIDIZED BED

Cole, W. E., and Sakhuja, R. K.

Thermo Electron Corp.
Waltham, Massachusetts, U.S.A.

The feasibility of using fluidized bed technology for glass batch preheating has been shown through Laboratory Testing. This technology provides over a 20 per cent energy reduction, a reduction in air pollution emissions, a reduction in furnace operating temperature (and consequently increased furnace life), as well as less than a two year payback period. To investigate the compatibility of the fluidization process with the glass manufacturing process, a laboratory scale heat exchanger has been built and tested. Testing has focused on the basic feasibility questions concerning the concept. Tests performed have verified:

- . the heat transfer performance;
- . the fluidization characteristics of glass batch;
- . the solids mixing and subsequent reduction of batch segregation;
- . the elutriation characteristics (loss of fine particles); and
- . that no deleterious effects, as indicated by laboratory crucible melts, are introduced by the fluidized bed.

ELECTRICAL THRESHOLD SWITCHING IN VANADIUM-TELLURITE GLASSES

Mansingh, A., Dhawan, V.K., and Jain, S.C.

University of Delhi, Delhi, India.

The dc current - voltage (I-V) characteristic of $V_2O_5 - TeO_2$ glasses in the composition range (20% to 80 % V_2O_5) and in the ambient temperature range (150K to 350K) has been measured in the sandwich structure using silver paint electrodes and a constant current source. The temperature of the sample surface has also been measured. The I-V characteristic is non-linear for small voltages ($<1V$) which may be attributed to the electrode barriers, followed by a linear region where bulk behaviour dominates. A nonlinearity region starts again at higher voltages followed by electrical breakdown and a negative differential resistance region. The electrical switching is reversible if the current is kept below a critical value. At higher values of current the sample goes to the memory state and the resistance remains low even on reducing the current. The surface temperature of the sample is only 8 to 10 degrees above the ambient at switching which strongly suggests the formation of a conducting filament. For the currents below the critical value, the temperature of the filament does not increase sufficiently high to cause phase change, and the X-ray analysis indicates that the sample remains amorphous. Above the critical value of the current when the sample goes to the memory state the filament temperature increases to the extent that phase change occurs and X-ray analysis of the samples shows the appearance of crystalline VO_2 . The threshold voltage (V_{th}) for reversible switching decreases and the threshold current (I_{th}) in unformed samples increases with increasing contents of V_2O_5 , increasing temperature and decreasing thickness but the critical power density at threshold ($V_{th} \times I_{th}$) shows very little variation (within 25%) for different ambient temperatures and composition of samples. The experimental data have been analysed in the light of existing theoretical models.

SESSION VI

ENVIRONMENT

THE EFFECT OF ENERGY AND ENVIRONMENTAL CONCERNS ON
THE GLASS CONTAINER INDUSTRY

Poole, J.P.

Brockway Glass Company, Inc.
Brockway, Pennsylvania, U.S.A.

Introduction:

The combined effects of the enactment of the National Environmental Policy Act in 1970, and the enormous increase in fuel cost resulting from the action of OPEC in 1973, have been extremely costly to the glass container industry.

R & D objectives have had to shift from those involving solutions to problems of glass technology and improved processing to finding out how to get permission to operate or construct facilities which will comply with the federal or local laws and, at the same time, hold fuel cost to a minimum by increased melting efficiencies.

Most glass companies were ill equipped to meet these new demands on their technical and operating personnel.

This paper will present a summation of the various types of legislation and regulations which resulted from the EPA and how they affect the glass industry. As the Clean Air Act probably has had the greatest impact on our industry, it will be treated in considerable detail. While the necessity for increased fuel efficiency is not a result of an Environmental Protection Agency (EPA) mandate, the quantity and type of melting fuels do have an important influence on the generation of particulates and gaseous emissions. This relationship is also included.

I Environmental Laws and Regulations:

The following laws and regulations were in effect in 1981. While some changes or modifications to these regulations are anticipated, it is thought that these changes will involve more extension of the period of time to achieve compliance than a reduction in the requirement of the rules themselves.

1. The Clean Air Act of 1970.
2. The Clean Water Act of 1977 amending the Federal Water Pollution Act of 1972.
3. The Resource Conservation and Recovery Act of 1976.
4. The Federal Toxic Substances Control Act of 1976.
5. Safe Drinking Water Act of 1974.
6. Hazardous Materials Transportation Act of 1975.
7. Federal Pesticide Control Law of 1972.
8. The Ocean Dumping Act of 1972.
9. Surface Mining Control and Reclamation Act of 1977.
10. Noise Control Act of 1972.
11. Federal Land Use Laws.
12. Federal Wild Life Protection Laws
13. Consumer Product Safety Act.

Obviously, some of this list affects us more than others. Some of them would not be expected to affect us if reasonable caution is maintained, but the fact is that all have the potential and consequently the industry must be aware of them. For example, one would assume that the Federal Pesticide Control Law would be of no consequence to the glass industry. The fact is that the definition of pesticide is so broad that it includes slimeicides and fungicides which are used by our plants as water treatment chemicals. Chlorine, as everyone knows - the common water treatment chemical, may be considered a pesticide if improperly handled. We could potentially even violate one of the wild life protection laws if migratory fowl were injured or killed landing on our cooling water ponds. Brief summaries of the Acts that affect the glass industry on a daily basis are included. These laws have spawned a host of federal regulations with more being promulgated almost daily. These regulations are staggering in their numbers and in many cases bewildering in their complexity.

II Clean Air Act:

While all of the Acts listed in I above affect the glass industry, it is the Clean Air Act which has received the most attention and publicity. While Pittsburgh, Pa., in the 30's was probably the first or earliest city to be concerned with air pollution, it was primarily the steel industry that was affected.

Los Angeles, because of its smog problem, has had local laws and regulations intended to reduce or minimize air pollution for many years well before EPA. The fact that our company had a plant located in Los Angeles county made it necessary for Brockway to learn what the operating variables controlling particulate and gaseous emissions were in order that the plant could be operated or expanded and remain in compliance with or without abatement equipment. This initial work, begun about 1965, has resulted in a whole host of experimental studies all of which have been published. A summary of this experimental work is presented.

As the air pollution regulations vary considerably from state-to-state and district-to-district, a table is presented showing the wide variation that currently exists in the limits for gaseous and particulate emissions. Also included is a table showing the change in design and fuel efficiency of Brockway furnaces over the last 30 years.

Many of the design modifications of the last 10 years have been accelerated because of demands of fuel cost and the Clean Air Act. One of the most costly and troublesome aspects of the Clean Air Act and the EPA is the requirement that a detailed application which includes an estimate of the emissions be filed for every new or modified facility that is planned in order that the local air pollution control authority can issue a permit for the furnace. This then must be followed by a permit to operate the furnace after the facility has been demonstrated to fall within the emission estimates originally predicted. Permits to operate might be required for existing sources which also

require estimates of emission rates. This obviously requires a quantitative knowledge of the emissions that will result from furnaces of different capacity and from different glass compositions and color well in advance of actually deciding to construct one. This is essential in order that it can be determined whether the furnace can be operated in compliance by making modifications to the operating process itself and design of the furnace, or whether an abatement device must be included in it.

To clarify the complication of securing permits to build a new furnace, a case history is presented of our negotiations with The Bay Area Air Pollution Control Board in Oakland, California, which finally lead to a construction and operation of an amber furnace, Tank 21.

III Conclusions:

A summation of those factors which affect particulate and gaseous emission rates from both flint and amber glasses are as follows:

Flint Glass:

1. In order to reduce particulate emissions:
 - a. Utilize carbon, sulfate fining
 - b. Increasing melting area or decrease production rate
 - c. Reduce melting and tank temperatures*
2. Reduce NO_x by:
 - a. Control the gas/air ratio
 - b. Reduce fossil fuel usage
 - c. Temperature reduction*
3. Reduce SO_2 by:
 - a. Change in batch or glass composition involving sulfur compounds**
 - b. Decrease in production rate

Amber Glass:

1. Reduce particulates by:
 - a. Decrease in production rate
 - b. Reduce melting and tank temperature*
2. Reduce NO_x by:
 - a. Control of gas/air ratio
 - b. Reduce fossil fuel usage
 - c. Temperature reduction*
3. Reduce SO_2 by:
 - a. Change in the batch or glass composition involving sulfur compounds**
 - b. Decrease in production rate

While the use of electrical boost is listed as one of the alternatives, it should be stated here that because of its expense, Brockway does not use electric boost as a method of achieving compliance with air pollution regulations unless cost analysis indicates that it is less expensive than adding and operating abatement equipment. The results of this philosophy and policy are best stated by the fact that in approximately 40 glass container furnaces only 2, at the present time, are equipped with abatement devices. The rest have reached compliance in their local district by process control or process modification.

* Temperature reduction can be achieved by the use of electric boost and/or increased cullet usage.

** Obviously, if fuel utilized contains sulfur, a change in the fuels to a lower sulfur or to a different type of fuel, such as going from oil to gas, will reduce the SO_2 emissions. SO_2 emissions are independent of furnace temperature.

VITRIFICATION PROCESSES OF FISSION PRODUCTS SOLUTIONS

Bonniaud, R., Jouan, A., Mancouyoux, J.P. and
Sombret, C.

Commissariat a l'Energie Atomique
Site de Marcoule, France

The development of nuclear energy in all industrialized countries has made it necessary that a solution be found to the problems caused by the nuclear wastes.

The main countries concerned have chosen the process of incorporation of these waste products in the form of oxides in a vitreous phase.

The principal differences between the production of this vitreous phase and the conventional glass production processes are:

- The need of an evaporation step in order to incorporate in a vitreous phase nearly forty elements originally in the form of nitrates in solution;
- The relatively small quantities of glass to be produced; in most cases 10 to 100 kg/hour;
- The restraints imposed by working in a hostile environment requiring leak-proof systems, protection against radiation, and means of remote control systems which necessitate equipment with high reliability;
- The avoidance of generating any secondary waste products, solids, liquid or gaseous, in appreciable quantities.

The process studied until now in different countries can be classified in two general categories: those which permit evaporation, calcination and fusion of the glass in the same equipment, and those which separate evaporation and calcination from fusion. The former category uses

either metallic containers or ceramic furnaces. The latter has different equipment such as rotating cylinders, fluidized beds or heated spray towers for evaporation and calcination and either ceramic or metallic containers for fusion.

The French process known as continuous vitrification is presently the only one working on an industrial scale in Marcoule. It consists of a rotating cylinder for evaporation and calcination and a metallic container heated by induction for vitrification. The plants to be built at La Hague, at Windscale in the U.K., at Karlsruhe in Germany and at Mol in Belgium will use this technology.

EFFECTS OF POTASSIUM OXIDE AND BORIC OXIDE ON CRYSTALLIZATION OF β -WOLLASTONITE GLASS-CERAMICS

Kume, M.

Nippon Sheet Glass Co. Ltd., Itami City, Japan

Glasses based on the system $\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ are of considerable interest for the production of glass ceramic materials. The blast furnace slags, which consist essentially of lime, magnesia, alumina and silica, can be used as major raw material for the glass ceramics.

It is very important in the production of these glass ceramics to reduce a deformation in its crystallization process. Especially, in a continuous rolling process of the glass ceramic plate, the apparent viscosity during a heat-treatment, should be higher than about 10^{10} poise.

In this study, the effect of a number of oxides (Na_2O , K_2O , B_2O_3) as well as the effect of the nucleating agent zinc sulfide was investigated.

When both boric oxide and potassium oxide are added to the glass system $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{ZnS}$, the following effects are observed.

1. It is found that the presence of B_2O_3 and K_2O contributes to the remarkable promotion of crystallization of the glass and that the apparent minimum viscosity of the glass is the crystallization temperature range increases up to 10^{10} poise. This reduces the deformation of the glass body during the crystallization process.
2. The time for nucleation is very short. In fact, no special heat treatment is required for nucleation.

3. There is no need for a strongly reducing atmosphere when melting a glass batch. In conventional glass-ceramics in this system, a glass batch should contain a relatively large quantity of sulfur in the form of sulfide and should, therefore, be maintained in a strongly reducing condition. This leads to the formation of a large amount of scum and zinc oxide can be reduced to the metallic state to prevent the crystallization of glass.

GLASS FURNACE GAS FIRING PRACTICES TO REDUCE FUEL USAGE AND NOX EMISSIONS

Neff, G.C.

Combustion Tech. Inc., Orlando, Florida, U.S.A.

1. Introduction

Discussion focuses on proper selection and operation of gas burners for a particular type and size glass melting furnace to obtain the most economical fuel usage and the lowest NOX emissions. Factors related to this criteria are enumerated in detail.

2. Importance of Fuel Savings

- a. Price trends
- b. Fuel availability
- c. Fuel cost relationship to total glass cost

3. Requirements for NOX Emissions Control

- a. Legislative requirements
- b. NOX and particulant relations
- c. Furnace pull and NOX emissions
- d. Electric boost considerations (not detailed here)

4. Furnace Types Vs. Fuel Rates and NOX Emissions

- a. Regenerative type side-port - different firing positions
- b. Regenerative type end-port - different firing positions

5. Elemental Factors Related to Fuel Rates and NOX Emissions

- a. Inspired air
- b. Air use with gas firing
- c. Off-side firing cooling air
- d. Luminous vs. non-luminous flames
- e. Flame configurations (geometry)
- f. Firing positions
 - Through side of port
 - opposed
 - angled
 - Over port
 - Under port
- g. Gas and combustion air velocities
 - Ratios
 - Momentums
 - Turbulance
- h. Flame temperatures
 - Highest - effects NOX
 - Average - no effect on NOX
- i. Flame speed
- j. Combustion air
 - Excess air
 - Combustion air temperature
- k. Complete combustion

6. Conclusions: By illustration to a particular furnace.

Best selection and use of the elemental factors to enhance minimum fuel usage and minimize NOX generation.

SPECTROSCOPIC INVESTIGATIONS AND CHEMICAL DURABILITY STUDIES
OF LEAD RELEASE IN CERAMIC GLAZES CONTAINING TRANSITION METAL IONS

van Roode, J.H.G.*, Murthy, M.K.*, Hechler, J.J.**,
and Cole, K.C.**

* Ontario Research Foundation, Mississauga, Ontario, Canada

** National Research Council Canada, Montréal, Québec, Canada

Lead release from ceramic glazes is a problem of concern to the ceramic industry and to health authorities. It has been known for some time that the addition of certain transition metal oxides, notably copper oxide, to lead based glazes significantly increases the lead release of ceramic food ware.

Using commercial type glaze formulations we found that heat treatment greatly affects the chemical durability of the glazes. While prior to heat treatment commercial glazes with and without added copper oxide give lead release values of similar magnitude the copper containing glaze shows a significantly higher value after heat treatment at 600°C for 24 hours.

As part of an investigation into the structural basis of the lead release behaviour we have used Raman spectroscopy, Fourier Transform Infrared spectroscopy, optical absorption spectroscopy and differential thermal analysis. Both commercial type glazes and glass model systems were used in our investigations. Heat treatment was carried out on glasses in the systems PbO-SiO_2 and $\text{Na}_2\text{O-SiO}_2$ to which small quantities of transition metal oxides were added. Significant differences were found in the structures of these model systems in the presence and absence of these transition metal oxides.

The lead release behaviour of ceramic glazes containing transition metal ions will be correlated with the data from this study.

POLYMER PROTECTIVE COATINGS FOR GLASS

Ali Zaida^(x), S., and Levenson^(xx), L.L.

(x) Glass Containers Corporation, Knox, Pennsylvania, U.S.A.

(xx) University of Colorado, Colorado Springs,
Colorado, U.S.A.

A series of polymer coatings are described for single step application to glass containers. These coatings are 1000-2000 Å thick. They improve the abrasion resistance and lubricity of the glass surface. The improved surface properties decrease breakage of the containers during handling, thus improving service life. The coatings are produced from an aqueous mixture of a poly-aminoacrylate ester, carnauba wax, and a vinyl amino silane coupling agent. The aqueous mixture is sprayed onto the glass containers as they exit from an annealing Lehr at a temperature between 200° - 400°F. It is shown that coatings of this type produce dry and wet lubricity and scratch resistance comparable to that of conventional coatings composed of bilayers of metal oxide (tin or titanium) and an organic resin. Furthermore, the two step processes required for bilayer coatings are simplified to one step, and the generation of hydrogen chloride vapor associated with the tin and titanium oxide coatings is avoided. The adhesion strength of the polymer coatings is shown to depend on the amount of silane coupling agent used. Autoclaving the container does not significantly change the polymer adhesion, even though sodium is leached from the glass surface during the leaching process, as revealed by ESCA. In-depth ESCA profiles of the polymer films reveal how the interface composition varies with different polymer mixtures.

POSTER SESSION

THE INFRARED AND RAMAN SPECTRA OF POTASSIUM BOROGERMANATE GLASSES

Chakraborty, I., and Condrate, Sr., R.A.

New York State College of Ceramics
at Alfred University
Alfred, New York, U.S.A.

Infrared and Raman spectroscopy have been used to obtain structural information concerning $K_2O-B_2O_3-GeO_2$ glasses. Changes occur in the coordination of boron (three to four) and germanium (four to six) upon addition of alkali oxide, similarly to $K_2O-B_2O_3$ and K_2O-GeO_2 glasses. The concentrations of the various borate and germanate groups appearing in the network depend upon the composition of glass. Structural changes for these groups occur at much higher K_2O/B_2O_3 and K_2O/GeO_2 molar ratios than for either borate or germanate glasses. At high B_2O_3 concentrations, boron undergoes a preferential coordination change over germanium. At moderate to high germania-concentrations, simultaneous changes occur in the coordination of both boron and germanium. This investigation also suggests that at higher alkali oxide concentrations non-bridging oxygen atoms are preferentially found on germanate groups rather than on borate groups. Borate groups containing two BO_4 -tetrahedra are not found at glass compositions relating to those of $K_2O-B_2O_3-SiO_2$ glasses for which such groups are found. The structural information regarding the changes in the coordination of boron and germanium atoms determined in the network of $Na_2O-B_2O_3-GeO_2$ glasses by Reibling et al., on the basis of physical properties such as partial molar volume and viscosity are consistent with those obtained in the present spectral investigation.

THE CHEMISTRY OF URANIUM IN GLASS-FORMING MELTS: REDOX INTERACTIONS OF URANIUM WITH CHROMIUM AND IRON IN ALUMINOSILICATES

Schreiber, H.D.¹, Balazs, G.B.^{1,2}, and Kozak, S.J.³

¹Department of Chemistry, Virginia Military Institute, Lexington, Virginia, U.S.A.

²Department of Chemistry, Washington & Lee University, Lexington, Virginia, U.S.A.

³Department of Geology, Washington & Lee University, Lexington, Virginia, U.S.A.

Systematic series of two calcium-magnesium-aluminosilicate glasses, (1) containing both uranium and chromium simultaneously in various molar ratios and (2) containing both uranium and iron simultaneously in various molar ratios, have been prepared at a melt temperature of 1500°C as a function of imposed oxygen fugacity in order to investigate the re-arrangements via internal redox reactions in the separate U(VI)-U(V)-U(IV), Cr(VI)-Cr(III)-Cr(II), and Fe(III)-Fe(II) equilibria in the glass-forming melts. In the uranium-chromium doped melts, the reactions,



occur to completion under oxidizing synthesis conditions, whereas the reactions,



also occur to completion under reducing synthesis conditions. Within experimental error, the Fe(III)-Fe(II) redox couple appears to have little, if any, systematic effect on the uranium redox equilibria. The distribution of uranium redox states in iron-containing glasses under relatively oxidizing synthesis condition is unaffected by the presence of iron.

Further contrast in the mutual interactions of uranium redox states in the same glass-forming melts is shown by a previous study in which Ce(IV)-Ce(III) did not interact with U(IV) but the reaction,



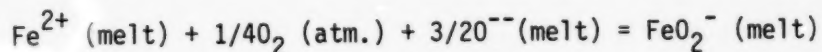
occurred albeit not to completion. The driving force for the degree of mutual interaction may be in the stability of the molecular associations formed within the melt (glass) microstructure by the reactions. Complexes such as Cr(III)-O-U(VI), Cr(III)-O-U(IV), Ce(III)-O-U(VI), and Ce(III)-O-U(IV) probably exist within the glass structure as a result of the internal redox reactions.

OXIDATION EQUILIBRIUM OF IRON IN BOROSILICATE GLASS

Goldman, D.S.

Owens/Corning Fiberglas Corporation
Granville, Ohio, U.S.A.

Ferrous/ferric equilibria have been determined in alkali-alkaline earth-borosilicate glass as a function of temperature, oxygen partial pressure and glass composition. Expected linear relationships are found between $\log(\text{Fe}^{2+}/\text{Fe}^{3+})$ and $\log(p\text{O}_2)$ or $1/T$. The slopes of the correlation with $\log(p\text{O}_2)$ are close to the expected value of -0.25, but are found to increase with increasing temperature. Reaction enthalpies determined from the correlation with $1/T$ of -24 to -28 kcal/mole are similar to those reported for other silicate glasses. The ferrous/ferric equilibrium is not dependent upon total iron content in the range 0.5 to 0.09% Fe_2O_3 . Experimental results indicate that the rate of oxidation is faster than the rate of reduction in these glasses. More reducing conditions are required at lower temperatures to stabilize the amber chromophore. The ferrous/ferric equilibria have been correlated to the number of bridging and non-bridging oxygen ions in the glass. The results suggest that the oxidation-reduction reaction can be written as:



AN INDIRECT ATOMIC ABSORPTION TECHNIQUE FOR THE DETERMINATION
OF TRACE AMOUNTS OF SULPHUR

Boulos, M.S.

Owens/Corning Fiberglass Corporation
Granville, Ohio, U.S.A.

A sensitive and precise analytical method has been developed for the measurement of trace amounts of sulphide compounds in glass and raw materials. The method is based upon the absorption of the hydrogen sulphide gas, evolved as a result of sulphide reaction with acid, into a dilute standard solution of silver nitrate. The amount of silver remaining unreacted in solution is then measured by atomic absorption spectrophotometry. Addition of a suitable reducing agent allows for the determination of total sulphur in the sample.

The apparatus required is simple and the method is fast, allowing for the analysis of a large number of samples in a short time. The detection limit for the technique is 0.001% sulphide-sulphur.

DYNAMIC FATIGUE TESTING OF WINDOW GLASS

Johar, S.⁽¹⁾ and Murthy, M.K.⁽¹⁾, Dalgleish, W.H.⁽²⁾

1. Ontario Research Foundation, Mississauga, Ontario, Canada.
2. National Research Council Canada, Ottawa, Ontario, Canada.

A unique testing facility has been designed and built at the Ontario Research Foundation (ORF) for the National Research Council, to investigate the important problem of how the strength of full-sized windows varies for different loading rates, using simulated but realistic wind gust pressures.

The test chamber consists of a front vertical panel with an opening 1.5 m x 2.4 m; a back panel containing a circular piston 2.4 m in diameter; and an airtight enclosure. The glass panel to be tested is mounted in the opening, and is held in place against a neoprene gasket with a known, uniform clamping pressure.

A hydraulic ram pulls the large piston backward under control of an electric system which senses the pressure drop inside the chamber; this pressure drop produces the load on the glass panel. The loading rate can be varied from 0.0025 kN/m²/s to 35 kN/m²/s (0.05 psf/s to 700 psf/s). Maximum pressures in the neighbourhood of 18 kN/m² (375 psf) are possible, greatly exceeding the normal range of pressures and suctions for cladding design.

The current study, supported and directed by three major glass manufacturers and the Division of Building Research of the National Research Council Canada, in addition to helping to evaluate the capabilities of the equipment, is expected to lead to more extensive research on the structural performance of glass as a cladding material, and possibly to investigations of other cladding materials.

THE USE OF SURFACE ACOUSTIC WAVES TO DETERMINE THE STRESS INTENSITY FACTOR IN GLASS

Fahr, A.⁽¹⁾, Johar, S.⁽¹⁾ Murthy, M.K.⁽¹⁾, Sturrock, W.R.⁽²⁾

1. Ontario Research Foundation, Mississauga, Ontario, Canada
2. Defense Research Establishment Pacific, Victoria, British Columbia, Canada.

High Frequency surface acoustic waves have been used to predict the maximum stress intensity factor of surface cracks in glass. Rayleigh waves were generated on plate glass specimens containing controlled surface cracks by placing a focus piezoelectric transducer in angle with respect to the specimen immersed in water. The maximum stress intensity factor of the surface cracks was inferred by measuring their acoustic reflection coefficient. The fracture stress of the specimens containing the acoustically characterized cracks was then measured in 4-point bending. The values of the fracture stress predicted from acoustic data were comparable to the values obtained by mechanical testing.